AD-A251 880

ON PAGE

may 27, 1992 | Technical Report #11

4. TITLE AND SUBTITLE Unexpected Redox Rectification by an Electrochemically Prepared Iridium Oxide Electrode/Aqueous Acid Interface

5. FUNDING NUMBERS

6. AUTHOR(S)

Christopher S. Johnson and Joseph T. Hupp

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Northwestern University
Department of Chemistry
2145 Sheridan Road
Evanston, IL 60208-3113

8. PERFORMING ORGANIZATION REPORT NUMBER

#11

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

DTIC
ELECTE
JUN 0 8 1992
S   A   D

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

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12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

In highly acidic aqueous solutions, electrochemically prepared iridium oxide films behave as steady-state insulators and transient rectifiers towards the $Ru(NH_3)_6^{3+/2+}$ redox couple. In less acidic solutions the films show only partial transient rectification or else fully reversible transient behavior, together with Koutecky-Levich type steady-state behavior. Experimental studies as a function of $Ru(NH_3)_6^{3+}$ concentration, solution pH, film thickness, voltammetric sweep rate and electrode rotation rate show that these unusual phenomena are related to: (1) transient uptake of $Ru(NH_3)_6^{3+}$, apparently in place of H^+, during film-based Ir(IV/III) cycling, (2) Donnan exclusion of $Ru(NH_3)_6^{3+}$ from the reduced film under steady-state conditions and/or (3) film-based diffusional inhibition of $Ru(NH_3)_6^{3+}$ reduction.

14. SUBJECT TERMS

15. NUMBER OF PAGES
25

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
unclassified	unclassified	unclassified	

NSN 7540-01-280-5500

53 85

OFFICE OF NAVAL RESEARCH

TECHNICAL REPORT

FOR

Grant N00014 91 J 1035

R & T Code 413302S

Technical Report No. 11

Unexpected Redox Rectification by an

Electrochemically Prepared Iridium

Oxide Electrode/Aqueous Acid Interface

Christopher S. Johnson
and Joseph T. Hupp*

Dept. of Chemistry
Northwestern University
Evanston, IL 60208

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Introduction

Electrochemically prepared iridium oxide films have attracted attention because of their electrochromic properties[1-4], their superiority as water oxidation catalysts[5-8], and their intrinsic redox chemistry[9-20]. We have been interested in the last feature from the point of view of unusual interfacial reaction pathways (e.g. surface redox-mediated oxidations of solution-phase species, electrochemical hydride transfers or atom transfers, etc.). We reasoned that the known electrochemical accessibility oi ɪridium (film) oxidation states **III, IV** and, apparently **VI**[7,8], and the coupling of these to proton uptake and release[9-20], would provide a chemical basis for unusual interfacial reactivity. Indeed, preliminary studies of both methanol and ascorbate electro-oxidation at iridium oxide (unpublished) have suggested the occurrence of unconventional reaction mechanisms.

For irreversible organic oxidations the overall electrochemical behavior is fairly complex, reflecting both the multielectron nature of the solution-phase chemical transformation (e.g. methanol to formate or CO_2, etc.) and the inherent electrochemical complexity of the film itself. In order to learn more about the latter, we decided to examine a very simple inorganic reaction: the one-electron reduction and re-oxidation of the ruthenium(III) hexaammine cation. Note that $Ru(NH_3)_6^{3+}$ is substitutionally inert and that its formal reduction potential (E_f) is close to the potential for the film-based iridium (IV/III) couple; note further that

the iridium couple is pH-dependent; for example[2]:

$$Ir(OH)_3 = Ir(O)(OH)_2 + H^+ + e^- \text{ (metal electrode)} \qquad (1)$$

The proximity of the two redox potentials was deemed interesting because the iridium(III) oxide is nominally insulating, while the Ir(IV) form is an electronic conductor[13]. We were hopeful, therefore, that $Ru(NH_3)_6^{3+}$ could serve as a simple probe of the potential dependent (pH dependent), *electrochemical* conductivity of the oxide film (i.e. ability of the film to deliver oxidizing or reducing equivalents to solution species).

Our preliminary observations point to much more interesting behavior. For example, at pH = 2 or higher, seemingly simple, reversible $Ru(NH_3)_6^{3+/2+}$ cyclic voltammetry is observed. At pH = 0, however, transient *rectifying* behavior is seen (i.e. only reduction is seen by cyclic voltammetry; see also ref. [21]). Further studies indicate that this unusual effect is related microscopically to the uptake of cations during film reduction. Finally, steady-state experiments, as both a function of pH and film thickness, show that electrochemical reduction actually occurs at the underlying metal — the film itself functioning (depending on pH) as either a diffusional barrier or a Donnan exclusion membrane.

The purpose of this report is to outline in brief form our experimental observations and to suggest a mechanism for the unusual reactivity patterns.

EXPERIMENTAL

Aqueous sulfuric acid (1.0M) and trifluoromethanesulfonic (triflic) acid (0.1 and 0.01M) solutions were prepared from the concentrated acids (Mallinckrodt and Alfa Chemicals, respectively) by using distilled water which had additionally been passed through a Barnsted Millipore NANO pure puriifcation system. The ionic strength of the most dilute triflic acid solution (pH = 2) was adjusted to μ = 0.1 by addition of 0.09M sodium triflate which had been prepared via neutralization of triflic acid with sodium bicarbonate. The pH's of other solutions were maintained with buffers, as follows: acetic acid/acetate (pH = 3.8), sodium hydrogen phosphate/disodium hydrogen phosphate (pH = 7.0) and sodium borate (pH = 9.7). $[Ru(NH_3)_6]Cl_3$ and $[Ru(NH_3)_6]Cl_2$ were both supplied by Aldrich. Lanthanum perchlorate (hydrated) was obtained from GFS Chemicals. The iridium working electrode (ca. 1.0mm diameter, 99.9% Aesar) was constructed as a rotating disk (Hysol epoxy and teflon shroud) and designed to fit a Pine AFMSRX rotator. To remove prior films, the electrode was lightly sanded (moist 1200 grit SiC paper) before each new experiment. It was then polished with successively smaller particles of alumina (to 0.05 micron). In addition, to remove loose alumina particles, the electrode was briefly sonicated (distilled water) following each polishing step.

Both cyclic and rotating disk voltammetry were performed in conventional two-compartment cells featuring a platinum counter electrode and a saturated calomel reference electrode (SCE). All potentials are reported versus the SCE. Control of potentials was provided by either a Pine Instruments AFRDE4 or a

Princeton Applied Research 264A potentiostat. Experiments were recorded with a Houston Omnigraphics 2000 X-Y recorder.

RESULTS AND DISCUSSION

Oxide film growth and voltammetric behavior. Consistent with earlier reports[1-20, 22-26] repetitive scanning of the potential of a well polished electrode between +1.26V and -0.24V vs. SCE in 1M H_2SO_4 results in steady growth of an electroactive oxide film, as suggested by fig. 1. Typical cycling conditions (5 minutes at 5V/s) yielded films containing ~5 x 10^{-8} moles/cm^2 of electroactive iridium, based on integration of the Ir(III/IV) wave at ca. +0.7V. Other voltammetric features (fig.1) included: (1) small hydrogen adsorption peaks (underlying iridium metal) near -0.1 to 0.2V, (2) a region of very little current flow (insulating Ir(III)) encompassing -0.05 to +0.4V, (3) an Ir(III/IV) redox wave centered at about +0.7V, (4) a broad structureless charging region beginning near +0.8V, (5) a comparatively narrow set of peaks centered at +1.1V, and (6) a sharply increasing anodic current associated with the onset of water oxidation near +1.2V. The exact nature of features **4** and **5** is somewhat controversial. Assignments which we find appealing and internally consistent, however, are ones which ascribe feature **4** to the gradual oxidation (i.e. nonintegral charging, or metal-oxygen -dπ band depletion) of a material initially prepared (+0.8V) in oxidation state IV, and feature **5** to the discrete two-electron oxidation of specific

(perhaps oligomeric?) iridium(IV) centers. (Thus, two forms of iridium (IV) oxide are postulated[12,19,20].)

Integration of feature 5 (using feature 4 as a base line) suggests that it comprises a small minority (ca. 6 to 20%) of the total available metal oxide, where the variability in the estimate reflects both film preparation conditions and film history. (For example, films grown at 100mV/s exhibit proportionately less of feature 5 than those grown at 5V/s, while aged films exhibit preferential loss of this feature. Thermally prepared films[27], on the other hand, seem to lack this feature altogether.)

Transient redox studies. Figure 2a shows the cyclic voltammetric response of 10mM $Ru(NH_3)_6^{3+}$ at pH = 2 at an iridium oxide surface. A more-or-less ideal, reversible wave is observed, *apparently* indicating good film electrochemical conductivity in the vicinity of the $Ru(NH_3)_6^{3+/2+}$ formal potential (-250mV). Figure 2b, obtained at pH = 1, also shows a reversible response but additionally shows an apparently irreversible pre-peak (-190mV). Finally, at pH = 0 (fig. 2c), only an irreversible peak is seen. The same experiment with $Ru(NH_3)_6^{2+}$ yields no electrochemical response, even though oxidation of the complex is thermodynamically favored over much of the potential range. Evidently *at this pH the film is behaving as a transient electrochemical rectifier* (cathodic current flow only).

Follow up experiments as a function of sweep rate, v, show that the peak current (i_p) increases linearly with v — clearly indicating that the reactant must be confined at the interface. Measurement of the peak potential as a function of sweep rate yield: $\partial E_p/\partial \log v$ = -70mV/decade (slight curvature is evident; see fig. 3).

As shown by fig. 4, the magnitude of i_p is also strongly dependent on the positive reversal potential in the voltammetric scan. Comparison to fig. 1 shows that the peak is seen only when the potential has previously been scanned through at least some portion of the Ir(III/IV) wave. Repetitive scan experiments further indicate that the positive potential excursion is required prior to *every* reductive scan for which the hexaammine ruthenium peak is to be observed. Figure 5 illustrates more quantitatively the relationship between $Ru(NH_3)_6^{3+}$ reactivity and Ir(III) oxidation. Shown is a plot of Q_{Ru} (the amount of reductive charge passed) and Q_{Ir} (the amount of film oxidation charge passed). The plot exhibits two linear regions, one with a unitless slope of 0.75 and the second with a slope of zero. Evidently only the most readily oxidizable iridium film sites (i.e. approximately the first 20%) are effective at binding $Ru(NH_3)_6^{3+}$, implying again that more than one type of metal-oxide site exists.

Returning to fig. 4, it can be seen that not only the peak current but also the peak potential, $E_{p,c}$, changes with the positive reversal potential for the voltammetric excursion. While the peak shift, and its apparent relationship to film loading, might be interpreted in terms of uncompensated (film) resistance effects (recall that the oxide is electronically insulating in this region), at least one

other interpretation is possible. Figure 6a shows that a plot of $E_{p,c}$ versus log Q_{Ru} (i.e. film concentration) is linear with a slope of -57 mV. Given that the solution concentration of $Ru(NH_3)_6^{3+}$ is unchanging in these experiments, we tentatively ascribe the peak shifts to a Donnan potential (see below).

Finally, an attempt was made to determine the dependence of the extent of film loading (integrated rectification current, Q_{Ru}) on the concentration of $Ru(NH_3)_6^{3+}$ in solution. We observed *no* loading dependence between 1 and 14mM; evidently the partition equilibrium lies completely to the left at all accessible concentrations.[*] As shown in fig. 6b, however, we did observe a systematic shift in $E_{p,c}$ versus log $[Ru(NH_3)_6^{3+}]$. The relationship is linear with a pseudo-Nernstian slope of +67mV (i.e. opposite in sign to that in fig. 6a).

Control experiments with $[Ru(NH_3)_6](PF_6)_3$ in place of $[Ru(NH_3)_6(Cl)_3$ showed no changes in electrochemical response. On the other hand, controls with the electroinactive La^{3+} in place of the ammine complex showed, as expected, no electrochemical response in region 2.

Steady-state redox studies. To complement the transient studies, a series of steady state (rotating disk voltammetry) studies was undertaken. Experiments at pH = 0 showed that the film is completely blocked towards sustained $Ru(NH_3)_6^{3+}$ reduction. At pH = 7, on the other hand, well defined limiting currents (i_{lim}) are seen. Furthermore, the currents vary with the square-root of rotation rate (ω) and

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[*]The lower solution concentration limit was determined by the extent of negative shift of $E_{p,c}$. Below 1mM, $E_{p,c}$ overlapped severely with current from hydrogen evolution.
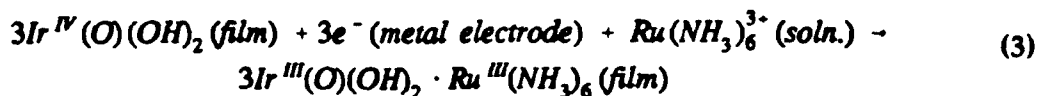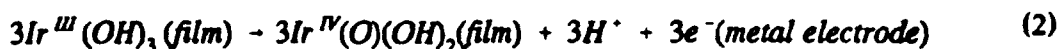
are equal (at all rotation rates) to the i_{lim} values seen at a nominally bare iridium metal surface. In view of these results it is tempting to ascribe the reactivity to some sort of residual conductivity in the reduced oxide at this pH. Consistent with that suggestion, the Ir(IV/III) wave (i.e. conductor/insulator transition) is in much closer proximity to the ruthenium couple at the higher pH. Additional experiments at intermediate pH's (fig. 7), however, cast doubt on this interpretation. At pH = 3.8, for example, Levich type behavior (linear i_{lim} vs. $\omega^{1/2}$ plot) is observed only up to rotation rates of about 100 r.p.m.; at higher rates i_{lim} is significantly less than the extrapolated Levich current. Behavior of this type is usually indicative of slow *chemical* kinetics of some type. Indeed, the data in fig. 7 can be fit satisfactorily to Koutecky-Levich plots (i_{lim}^{-1} vs. $\omega^{-1/2}$), where the inverse intercepts of the plots provide measures of chemical reaction rates[28]. Analysis for $Ru(NH_3)_6^{3+}$ reduction yields progressively larger intercepts (i.e. smaller inverse intercepts, currents (i_{KL}) or rates) as the pH is increased.

Behavior of this type conceivably could still be consistent with pH-dependent changes in residual film conductivity. Another explanation, however, is that the oxide is electronically insulating in this potential range (as expected), but that it is permeable to the ruthenium cation. If reduction ultimately occurred rapidly at the underlying metal surface, then the rate-limiting chemical process would be diffusion through the oxide film[29,30]. Strong support for this interpretation is provided by fig. 8 (i_{lim} vs. $\omega^{1/2}$) which shows that at a constant pH,

the interfacial kinetics are significantly diminished by increasing the oxide-layer thickness.

Mechanistic Interpretation. The preceding steady-state experiments clearly demonstrate that the insulating iridium(III)oxide film can function, at least at some pH's, as a cation permeable membrane. Coupling of the Ir(III/IV) reaction (eq.1) to proton release and uptake further suggests that the film might display ion-exchange properties.[*] To rationalize the initial electrochemical findings (figs. 2 and 4), therefore, we propose the following:

Scheme 1

$$3Ir^{III}(OH)_3 \, (film) \rightarrow 3Ir^{IV}(O)(OH)_2(film) + 3H^+ + 3e^-(metal \; electrode) \quad (2)$$

$$3Ir^{IV}(O)(OH)_2 \, (film) + 3e^- \, (metal \; electrode) + Ru(NH_3)_6^{3+} \, (soln.) \rightarrow$$
$$3Ir^{III}(O)(OH)_2 \cdot Ru^{III}(NH_3)_6 \, (film) \quad (3)$$

$$Ru(NH_3)_6^{3+} \, (film) + e^- \, (metal \; electrode) \rightarrow Ru(NH_3)_6^{2+} \, (film) \quad (4)$$

$$Ru(NH_3)_6^{2+} \, (film) + 2H^+ \, (soln.) \rightarrow Ru(NH_3)_6^{2+} \, (soln.) + 2H^+ \, (film) \quad (5)$$

Reactions 2 and 3 would clearly account qualitatively for the relationship (fig. 4) between extent of iridium oxidation and extent of binding of $Ru(NH_3)_6^{3+}$. Quantitative agreement, on the other hand, would require a greater proton to

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[*]Compelling evidence for non-protonic cation binding by electroactive iridium oxide (albeit, in nonaqueous solvents) has been reported by Glarum and Marshall [13] and by Pickup and Birss [31].

electron ratio in eqs. 2 and 3. For example, the alternative stoichiometry in eq. 6 would presumably lead to a Q_{Ru}:Q_{Ir} ratio of 0.67, in better agreement with

$$Ir^{III}(OH)_2(H_2O)^{\cdot}\ (film)\ \rightarrow\ Ir^{IV}(O)(OH_2)\ (film)\ +\ 2H^{\cdot}\ +\ 2e^-\ (metal\ eletrode) \tag{6}$$

experiment. While we are unaware of any additional data which support a proton:electron ratio as large as 2, we note that Burke and Whelan [14] have obtained evidence (E_f vs. pH) for ratios as large as 1.5. For our experiments it is conceivable that an even higher stoichiometry obtains for the apparently unique sites (ca. 20% of film total; see fig. 1) involved in $Ru(NH_3)_6^{3+}$ uptake.

Returning to Scheme 1, eqs. 3-5 imply the existence of a Donnan membrane potential which may be controlled, in part, by varying the ratio of $Ru(NH_3)_6^{3+}$ inside the film to $Ru(NH_3)_6^{3+}$ outside. The ability to vary these two concentrations independently (see fig. 6 and text) would lead to both positive and negative concentration-induced potential shifts [32,33] (fig. 6a and b) and to the following more general expression for $E_{p,c}$:

$$E_{p,c} = E_f\ (soln.) + \frac{RT}{nF}\ \ln\ \frac{[Ru(NH_3)_6^{3+}]outside}{[Ru(NH_3)_6^{3+}]inside} + constant \tag{7}$$

In eq. 7 the constant would include factors responsible for the electrochemical irreversiblity (see below) as well as concentration terms associated with other exchangeable ionic components of the electrolyte solution. Intuitively, eq. 7 would seem to be most applicable at fixed solution pH - conditions which are clearly met in our experiments.

Returning to Scheme 1, rapid irreversible kinetics for reaction 5 would account for the irreversible nature of reaction 4. If reaction 5 were *extremely* rapid, one might ultimately expect microscopic (i.e. interfacial) kinetic control of the overall electrochemical response via eq. 4. Ordinarily, the electrochemical kinetics of the $Ru(NH_3)_6^{3+/2+}$ couple would be regarded as too fast to measure by slow-sweep cyclic voltammetry. Note, however, that if eq. 5 were sufficiently rapid then $E_{p,c}$ for reaction 4 would be observed at significant *under*potentials, where Tafel kinetics would necessarily lead to diminished rates for electron transfer. While this "kinetic" interpretation is clearly speculative, it does account nicely for one remaining experimental observation: the very strong sweep-rate dependence of $E_{p,c}$. Assuming uncompensated film resistance effects can be neglected (a point still to be confirmed experimentally), standard voltammetry theory would predict a $\partial E_{p,c}/\partial \log v$ value of 59mV/α, where α is the transfer coefficient [3,4]. Figure 3 suggests a potential dependence for α, with an average α value of 0.84. Note that a transfer coefficient in excess of 0.5 would be expected if the kinetics of reaction 4 were being monitored at potentials well positive of the true reversible, film-based potentials (as we have speculated above). Finally, the direction of reaction 5 as written would also be consistent with the blocking nature of the metal oxide film towards $Ru(NH_3)_6^{2+}$ oxidation in highly acidic solutions.

More generally, the pH-dependent blocking/permeability behavior in steady-state experiments can be rationalized by recognizing the inherent pH dependence of the composition of the iridium (III) coordination sphere. While the exact nature

of the coordination environment is unclear, the pH dependence of the Ir(IV/III) redox potential (60 to 90mV/pH unit)[2,14] implies a 1 to 1.5 proton equilibrium for Ir(III) over the available pH range; for example:

$$Ir(OH)_2O^- + H^+ \rightleftharpoons Ir(OH)_3 \tag{8}$$

or from eq. 6:

$$Ir(OH)_2O^- + 2H^+ \rightleftharpoons Ir(OH)_2(OH_2)^+ \tag{9}$$

Note that reaction 9 (but not reaction 8) would impart pH-dependent cation exclusion (i.e. Donnan exclusion) characteristics to the electrode, as indeed observed experimentally (see fig. 7). Scheme 1, of course, provides a transient means for circumventing the Donnan exclusion effect, but would be ineffective in a steady-state experiment — again consistent with our observations. Finally, we suggest that while evidence for Scheme 1 is compelling only at lower pH's, the scheme (or at least reactions 2 and 3) could well be operative at higher pH's, but unobservable by transient methods because of overlap with the permeation-based reduction reaction.

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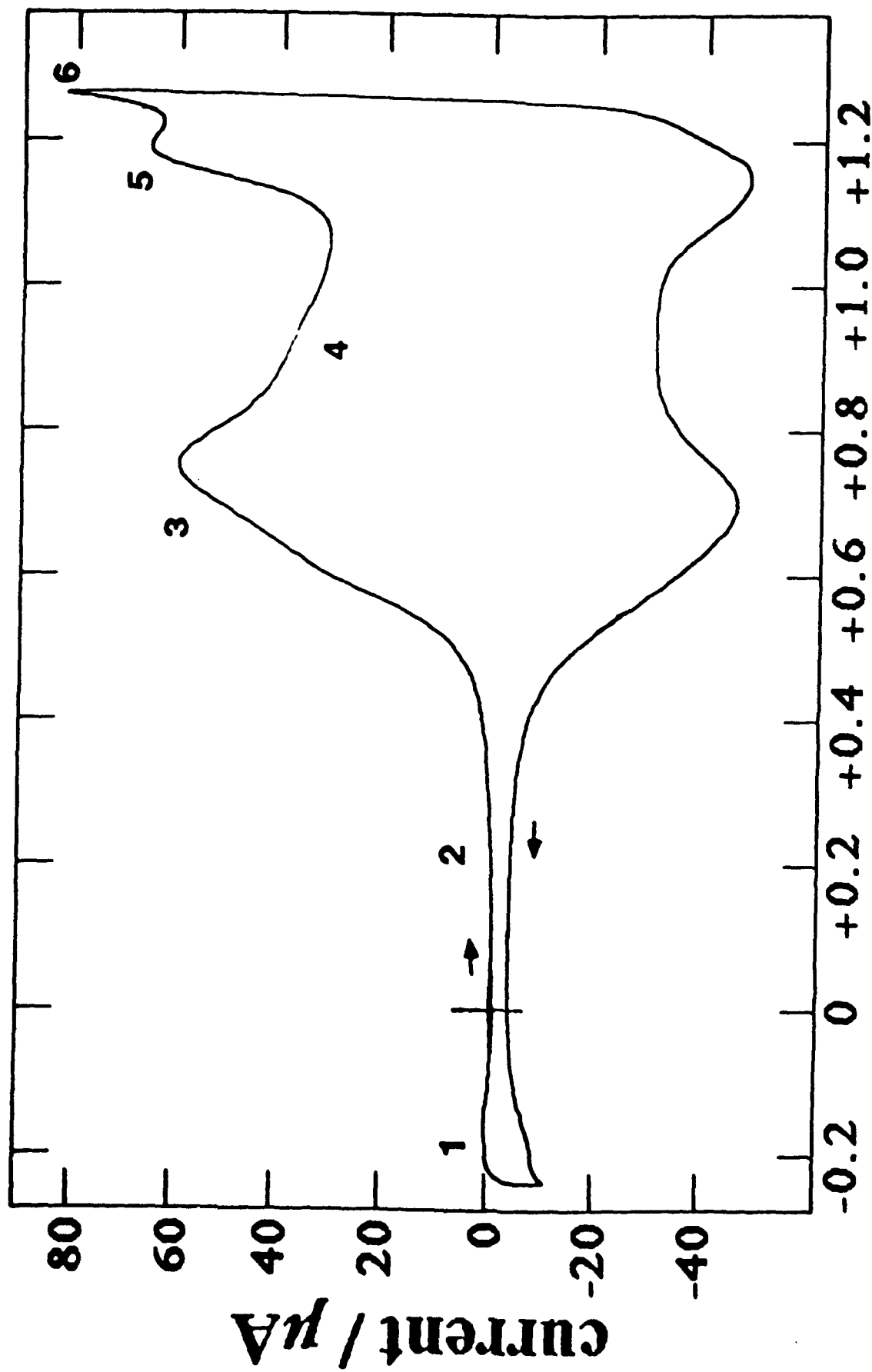20. L.D. Burke and E.J.M. O'Sullivan, J.Electroanal.Chem. 117(1981)155.

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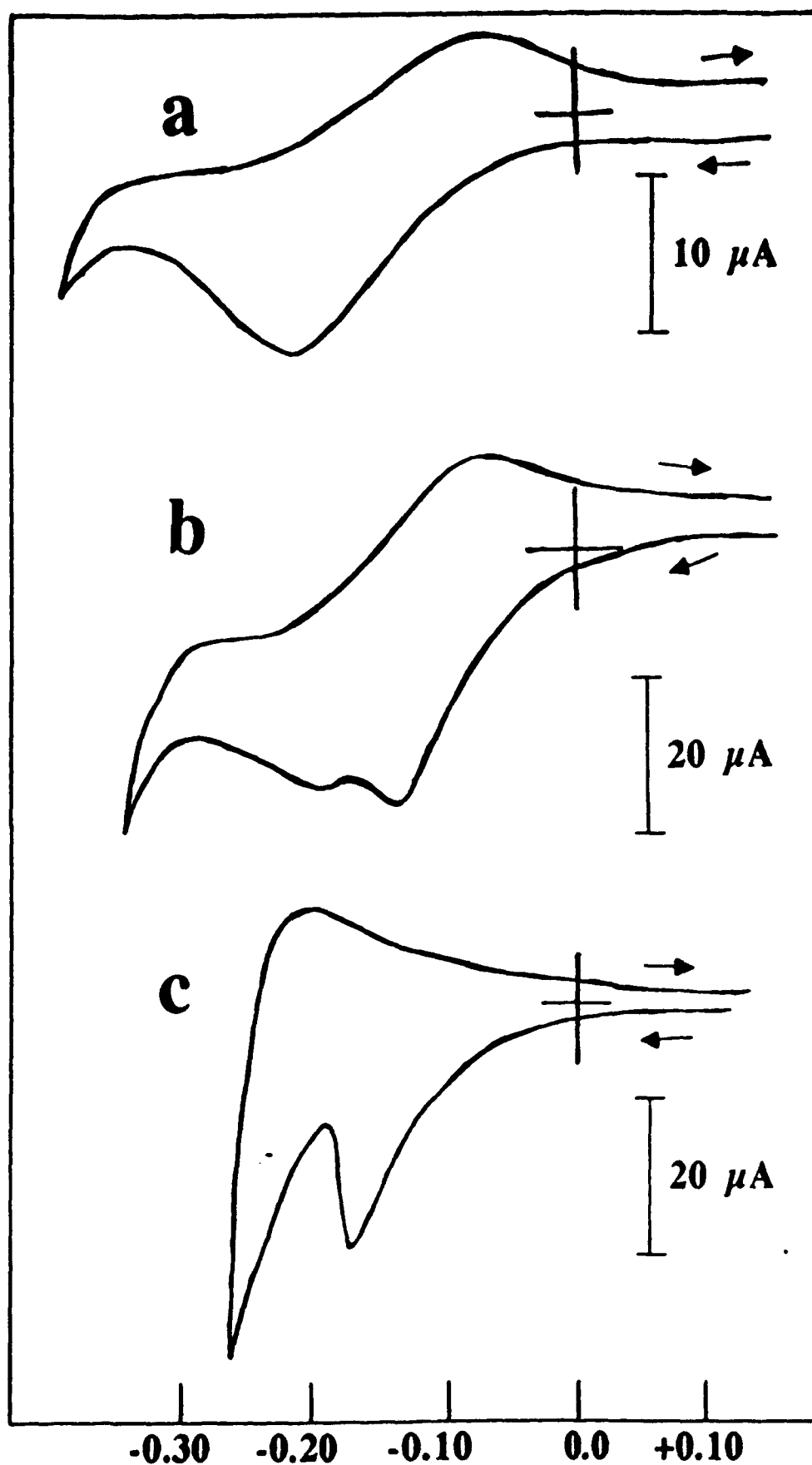
Figure Captions

1. Cyclic voltammogram (100mV/s) of a hydrous iridium oxide film in 1.0M H_2SO_4 solution. The film was grown on iridium metal by potential cycling (5V/s) between -0.24V and +1.26V vs. s.c.e. for 5 minutes (500 cycles). See text for a description of the characteristic features of the voltammogram.

2. Cyclic voltammetry (100 mV/s) of 5-10mM $Ru(NH_3)_6^{3+}$ at iridium oxide in contact with solutions at: (a) pH = 2, (b) pH = 1, and (c) pH = 0. The positive potential limit in each case was +0.5V. The oxide film was prepared by cycling 500 times at 5V/s between -0.24V and +1.26V vs. s.c.e.

3. Reductive peak potential versus log sweep rate (mV/s) for $Ru(NH_3)_6^{3+}$ at iridium oxide in 1.0M H_2SO_4.

4. Cyclic voltammograms (100mV/s) for reduction of film-based $Ru(NH_3)_6^{3+}$ in 1M H_2SO_4. The initial voltammogram (no Ru^{III} reduction current) features a positive reversalpotential of +0.4V. Subsequent voltammograms were obtained by progressively increasing the positive reversal potential by increments of +0.04V, up to +0.84V. The oxide film was prepared by cycling 500 times between -0.24V and +1.26V.

5. Q_{Ru} versus Q_{Ir} from cyclic voltammetry (100mV/s) in 1.0M H_2SO_4. The oxide film was grown by cycling 500 times between -0.24 and +1.26 at 5V/s. Charges were varied by increasing the positive potential limit in 0.04V increments, beginning at +0.44V ($Q_{Ir} < 2\mu C$) and ending at +0.84V ($Q_{Ir} = 108 \mu C$).

6. Pseudo-Nernst plots of $E_{p,c}$ versus $Ru(NH_3)_6^{3+}$ concentration, in 1M H_2SO_4. Panel (a): variable internal concentration (Q_{Ru}; taken from fig. 4) with fixed external concentration ($[Ru(NH_3)_6^{3+} = 7$ mM). Panel (b): variable external $Ru(NH_3)_6^{3+}$ concentration with fixed internal concentration ($Q_{Ru} = 16 \mu C$). Both oxide films were prepared by cycling 500 times between -0.24 and +1.26V at 5V/s.

7. Levich plots (i_{lim} vs. $\omega^{1/2}$) for the reduction of 10mM $Ru(NH_3)_6^{3+}$ at a rotating iridium oxide film electrode. The pH's of the solutions were 9.7(+), 7.0($\square$), 3.8(O), and 1.9(x). No current was observable at pH = 0. (The oxide film was grown with 900 cycles at 5V/s between -0.24 and +1.26V in 1M H_2SO_4.)

8. Levich plots (i_{lim} vs. $\omega^{1/2}$) for the reduction of 10mM $Ru(NH_3)_6^{3+}$ at a rotating iridium oxide film electrode at pH = 7.0. Thickness of the oxide was varied by systematically varying the number of growth cycles (linear relationship) from 200(+) to 400(O), 900($\square$), 1900($\lozenge$) and 3400(x). The cycling conditions are specified in fig. 7.

The vertical axis is labeled $\dot{i}_{lim}$ and the horizontal axis is labeled $\omega^{1/2} / (rpm)^{1/2}$.